

A practical synthesis of 3,4-diamino-6-azido-1*H*-pyrazolo[4,3- c]pyridin-5-ium energetic ionic compounds

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Experimental cautions

Cautions! Although there have been no explosions when dealing with these compounds, we strongly encourage to take strict precautions because of their relatively high energy and mechanical sensitivity. A protective goggle, protective masks and gloves must be worn at all times. The horn spoons should be used during the after-treatment process. Grinding should be avoided, if unavoidable, it is recommended to use an agate mortar, but also pay attention to the release of static electricity. All the compounds were dried under vacuum oven at 80 °C.

General methods

All reagents are purchased from Energy Chemical of analytical grade and were used strictly in accordance with regulations. Nuclear magnetic resonance (NMR) spectra were recorded using an AVANCE 500 Bruker spectrometer and chemical shifts were reported in ppm. IR spectrum were recorded using KBr pellets with a Thermo Nicolet iS10 spectrometer. The melting and decomposition (onset) points were measured on a differential scanning calorimeter (Mettler Toledo DSC823e) at a scan rate of 5 °C·min⁻¹. Densities were confirmed at room temperature by using the Micromeritics AccuPyc 1340 gas pycnometer. Impact and friction sensitivities were obtained using a standard BAM dropping hammer and a BAM friction Tester. High resolution mass spectra were obtained by using Thermo Fisher Q-Exactive-Focus LCMS. Elemental analysis was performed on Thermo Scientific FlashSmartTM instrument.

Computations

The gas formation enthalpies of these compounds are calculated by using the Gaussian 09 software¹ with the M06-2X function² and def2-TZVP basis set³.

For energetic salts, the solid-phase heat of formation is calculated based on a Born-Haber energy cycle (Figure S1).

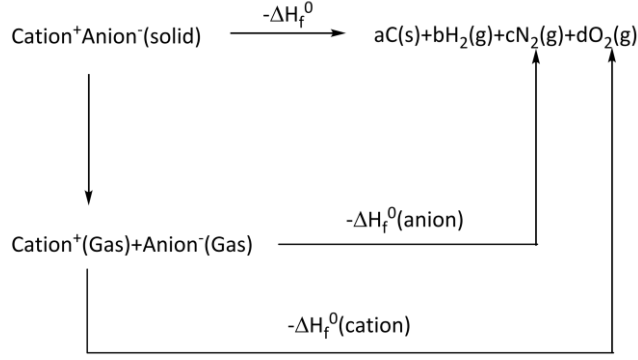


Figure S1. Born-Haber Cycle for the formation of energetic salts

The number is simplified by equation 1:

$$\Delta H_f^0(\text{salt}, 298\text{ K}) = \Delta H_f^0(\text{cation}, 298\text{ K}) + \Delta H_f^0(\text{anion}, 298\text{ K}) - \Delta H_L \quad (1)$$

Where ΔH_L is the lattice energy of the salts, which could be predicted by using the formula suggested by Jenkins et al [Eq. (2)].⁴

$$\Delta H_L = U_{POT} + [p(n_M/2 - 2) + q(n_X/2 - 2)]RT \quad (2)$$

Where n_M and n_X depend on the nature of the ions, M^{q+} and X^{p-} , and are equal to 3 for monatomic ions, 5 for linear polyatomic ions, and 6 for nonlinear polyatomic ions. The equation for lattice potential energy U_{POT} [Eq. (3)] has the form:

$$U_{POT} [\text{kJ} \cdot \text{mol}^{-1}] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (3)$$

Where ρ_m [$\text{g} \cdot \text{cm}^{-3}$] is the density of the salt, M_m is the chemical formula mass of the ionic material, the coefficients γ ($\text{kJ} \cdot \text{mol}^{-1} \cdot \text{cm}$) and δ ($\text{kJ} \cdot \text{mol}^{-1}$) are assigned literature values.

The solid-state enthalpy of formation for neutral compound can be estimated by subtracting the heat of sublimation from gas-phase heat of formation. Based on the literature,⁵ the heat of sublimation can be estimated according to supplementary equation (4), where SA is the surface area of the 0.001 electron/bohr³ isosurface of the electron density of the molecule, σ_{Tot}^2 is a measure of the variability of electronic potential on the surface, and v is the degree of balance between the positive and negative charges on the isosurface. The constants a, b and c are assigned literature values.

$$\Delta H(\text{Sublimation}) = a(\text{SA})^2 + b\sqrt{v\sigma_{\text{Tot}}^2} + c \quad (4)$$

$$\Delta H_{\text{g},4} = 499.78 \text{ kJ} \cdot \text{mol}^{-1}, \Delta H(\text{sub})_4 = 150.46 \text{ kJ} \cdot \text{mol}^{-1}$$

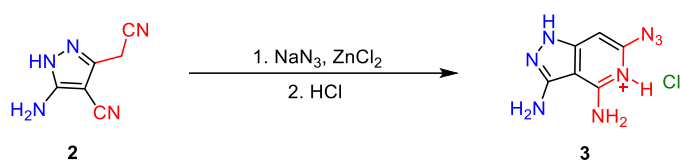
Calculation results are shown in Table S1.

Table S1. calculated lattice energies (ΔH_{Lat}) and the heats of formation of cation ($\Delta H_{\text{f}}^{\text{Cation}}$) and anion ($\Delta H_{\text{f}}^{\text{Anion}}$)

Compound	$\Delta H_{\text{f}}^{\text{Cation}}(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H_{\text{f}}^{\text{Anion}}(\text{kJ}\cdot\text{mol}^{-1})$	$\Delta H_{\text{Lat}}(\text{kJ}\cdot\text{mol}^{-1})$
5	-477.42	1259.13	484.3
6	-477.42	1686.97	456.0
7	-477.42	3134.91	978.2

Optimization of reaction conditions for the synthesis of compound 3

Compound 2 was firstly synthesized according to the known literature.⁶ To a round flask was added compound 2 (1.47 g, 10 mmol), H₂O (20 mL) and a stirred bar. NaN₃ and ZnCl₂ were then added into the flask at room temperature. The reaction mixture was heated and stirred for a certain time. After the mixture cooled down to room temperature, the precipitate was collected by filtration and washed repeatedly with water. The solid was then dissolved in a small amount of concentrated hydrochloric acid. The mixture was then left to standing overnight. The resulting solid was filtered and dried under the vacuum oven at 80 °C for 24 h to accessing the desired product 3.

Table S2. Optimized conditions for accessing compound 3^a

Entry	NaN ₃	ZnCl ₂	T/°C	Yield (%)
1	2.0 eq	2.0 eq	100	72
2	1.0 eq	2.0 eq	100	72
3	1.0 eq	1.0 eq	100	72
4	1.0 eq	-	100	0
5	1.0 eq	0.2 eq	100	7
6	1.0 eq	1.0 eq	80	25

^a Compound 2 (10 mmol), H₂O (20 mL), NaN₃, ZnCl₂, isolated yield after the vacuum drying.

Synthesis

6-azido-1H-pyrazolo[4,3-c]pyridine-3,4-diamine hydrochloride (3): To a round flask was added compound 2 (1.47 g, 10 mmol), H₂O (20 mL) and a stirred bar. NaN₃ (0.65 g, 10 mmol) and ZnCl₂ (1.36 g, 10 mmol) were then added into the flask at room temperature. The reaction mixture was heated to 100 °C and stirred for 10 h. After the mixture cooled down to room temperature, the precipitate was collected by filtration and washed repeatedly with water. The solid was then

dissolved in a small amount of concentrated hydrochloric acid. The mixture was then left to standing overnight. The resulting solid was filtered and dried under the vacuum oven at 80 °C for 24 h to accessing the desired product **3** as brown solid (1.63 g, 72% yield). **¹H NMR (500 MHz, DMSO-*d*₆)** δ 8.89 (s, 1H), 7.93 (s, 2H), 6.58 (s, 1H), 6.25 (s, 2H). **¹³C NMR (126 MHz, DMSO-*d*₆)** δ 152.35, 148.85, 147.81, 147.57, 92.36, 84.72. **IR (KBr):** $\tilde{\nu}$ =3401.39, 3187.19, 2910.78, 2147.50, 1659.67, 1615.95, 1542.50, 1453.77, 1318.30, 1260.20, 1145.37, 1044.86, 982.64, 840.62, 808.00, 751.68, 636.68, 596.43, 574.68, 493.47, 434.16, 419.62 cm⁻¹. Elemental analysis for C₆H₇N₈Cl (226.05): calcd. C 31.80, H 3.11, N 49.44%; found C 31.81, H 3.10, N 49.45%.

6-azido-1*H*-pyrazolo[4,3-*c*]pyridine-3,4-diamine (4): To a round flask was added compound **3** (2.26 g, 10 mmol), H₂O (10 mL) and a stirred bar. The sodium bicarbonate (0.84 g, 10 mmol) was dissolved in a small amount of H₂O and then added into the mixture. The reaction mixture was stirred at room temperature for 30 min. The resulting yellow solid was then collected by filtration and vacuum dried at 80 °C for 24 h to obtain compound **4** (1.09 g, 57% yield). **¹H NMR (500 MHz, DMSO-*d*₆)** δ 11.49 (s, 1H), 8.22 (s, 2H), 6.55 (s, 1H), 5.86 (s, 2H). **¹³C NMR (126 MHz, DMSO-*d*₆)** δ 149.62, 149.14, 147.07, 137.77, 93.03, 71.46. **IR (KBr):** $\tilde{\nu}$ =3429.25, 3331.59, 3158.01, 2220.99, 1637.68, 1598.25, 1559.97, 1540.11, 1512.53, 1484.95, 1427.43, 1406.05, 1359.21, 1330.85, 1291.93, 1269.50, 1229.04, 1194.12, 1139.19, 1122.64, 1061.11, 1032.15, 1020.24, 929.02, 856.91, 821.73, 786.00, 740.05, 714.00, 675.81, 656.12, 518.72, 450.81 cm⁻¹. Elemental analysis for C₆H₆N₈ (190.07): calcd. C 37.90, H 3.18, N 58.92%; found: C 37.88, H 3.20, N 58.91%. HRMS (ESI) *m/z*: [M-H]⁻ Calcd for C₆H₅N₈⁻: 189.0643, Found 189.0631.

3,4-diamino-6-azido-1*H*-pyrazolo[4,3-*c*]pyridin-5-ium nitrate (5): To a round flask was added compound **4** (0.38 g, 2 mmol) and a stirred bar. Then HNO₃ (7.5 mL, 10%) aq. was added slowly and the mixture was stirred at 50 °C for 30 min. After the mixture cooled down to room temperature, the resulting precipitate was collected by filtration and vacuum dried at 80 °C for 24 h to afford compound **5** as a brown solid (0.36g, 71% yield). **¹H NMR (500 MHz, DMSO-*d*₆)** δ 8.81 (s, 1H), 7.59 (s, 2H), 6.62 (s, 1H), 6.24 (s, 2H). **¹³C NMR (126 MHz, DMSO-*d*₆)** δ 149.76, 148.98, 147.37, 139.50, 92.63, 72.02. **IR (KBr):** $\tilde{\nu}$ =3385.32, 3243.32, 3164.89, 2221.53, 2151.04, 1685.94, 1634.11, 1592.08, 1540.13, 1426.82, 1386.07, 1343.23, 1298.76, 1249.90, 1229.98, 1179.44, 1109.47, 1040.47, 1011.24, 987.78, 913.89, 833.09, 784.82, 721.34, 698.61, 660.03, 564.49, 507.81, 459.54, 418.93 cm⁻¹. Elemental analysis for C₆H₇N₉O₃ (253.07): calcd. C 28.46, H 2.79, N 49.79%; found:

C 28.48, H 2.80, N 49.77%.

3,4-diamino-6-azido-1*H*-pyrazolo[4,3-*c*]pyridin-5-ium (*Z*)-5-(nitroimino)-4,5-dihydro-1*H*-tetrazol-5-yl)nitramide (6):

To a round flask with compound **4** (0.38 g, 2 mmol) and H₂O (5 mL) was added *N*-(1*H*-tetrazol-5-yl)nitramide (0.26 g, 2 mmol) and a stirred bar. The reaction mixture was heated to 100 °C and stirred for 30 min. The mixture was then cooled down to room temperature. The resulting precipitate was collected by filtration and vacuum dried at 80 °C for 24 h to afford **6** as a yellow solid (0.42 g, 65% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.33 (s, 2H), 7.26 (s, 1H), 6.55 (s, 1H), 6.11 (s, 1H), 4.18 (s, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ ¹³C NMR (126 MHz, DMSO) δ 149.64, 149.11, 148.44, 147.06, 137.79, 93.02, 71.47. IR (KBr): $\tilde{\nu}$ = 3431.63, 3336.61, 3264.66, 3167.62, 3094.17, 2988.17, 2900.90, 2222.64, 1661.01, 1635.38, 1599.92, 1560.27, 1539.02, 1485.71, 1428.27, 1406.73, 1331.01, 1269.87, 1228.34, 1194.83, 1142.91, 1122.54, 1065.54, 1043.18, 857.81, 821.44, 786.30, 689.56, 675.46, 656.76, 533.50, 452.10 cm⁻¹. Elemental analysis for C₇H₈N₁₄O₂ (320.10): calcd. C 26.25, H 2.52, N 61.24%; found: C 26.28, H 2.51, N 61.28%.

Bis{3,4-diamino-6-azido-1*H*-pyrazolo[4,3-*c*]pyridin-5-ium}4,4',5,5'-tetranitro-[2,2'-biimidazole]-1,1'-diide (7):

To a round flask was added compound **4** (0.38 g, 2 mmol), H₂O (5 mL) and a stirred bar. Compound 4,4',5,5'-tetranitro-1*H*,1'*H*-2,2'-biimidazole (0.31 g, 1 mmol) was then added into the mixture. The reaction mixture was heated to 100 °C with stirring. After another 30 min, the mixture was cooled down to room temperature, the precipitate was collected by filtration and vacuum dried at 80 °C for 24 h to afford **7** as a yellow solid (0.51 g, 79% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ 8.34 (s, 2H), 7.21 (s, 1H), 6.55 (s, 1H), 6.11 (s, 1H), 4.18 (s, 2H). ¹³C NMR (126 MHz, DMSO-*d*₆) δ 154.48, 149.67, 149.15, 147.10, 141.12, 139.35, 138.27, 71.63. IR (KBr): 3675.37, 3464.76, 3378.06, 3325.52, 2988.09, 2900.82, 2222.68, 2132.99, 1663.78, 1627.51, 1549.24, 1515.83, 1478.40, 1456.18, 1394.85, 1365.63, 1309.36, 1229.22, 1149.57, 1065.82, 958.96, 891.91, 854.48, 824.85, 810.26, 791.47, 771.76, 751.96, 698.39, 673.06, 601.65, 523.88, 451.90, 434.30, 418.54 cm⁻¹. Elemental analysis for C₁₈H₁₄N₂₄O₈ (694.14): calcd. C 31.13, H 2.03, N 48.41%; found: C 31.10, H 2.05, N 48.45%.

Crystal data

Table S3. Crystallographic data for **3·H₂O** and **5·H₂O**

Compound	3·H₂O	5·H₂O
Empirical formula	C ₆ H ₉ N ₈ OCl	C ₆ H ₉ N ₉ O ₄
Formula weight	244.66	271.22
Temperature/K	296(2)	296(2)
Crystal system	monoclinic	monoclinic
Space group	P2 ₁ /c	P2 ₁ /m
a/Å	6.9239(5)	9.2168(14)
b/Å	8.6109(6)	6.5123(11)
c/Å	17.0430(12)	10.2460(15)
α/°	90	90
β/°	93.587(2)	115.755(4)
γ/°	90	90
Volume/Å ³	1014.13(12)	553.90(15)
Z	4	2
ρ _{calc} /cm ³	1.602	1.626
μ/mm ⁻¹	0.372	0.138
F(000)	504.0	280.0
Crystal size/mm ³	0.26 × 0.23 × 0.2	0.15 × 0.01 × 0.01
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	5.302 to 55.04	4.414 to 54.974
Index ranges	-8 ≤ h ≤ 8, -10 ≤ k ≤ 11, -22 ≤ l ≤ 19	-11 ≤ h ≤ 11, -8 ≤ k ≤ 7, -13 ≤ l ≤ 13
Reflections collected	9212	6862
Independent reflections	2316 [R _{int} = 0.0246, R _{sigma} = 0.0230]	1383 [R _{int} = 0.0558, R _{sigma} = 0.0552]
Data/restraints/parameters	2316/3/157	1383/0/118
Goodness-of-fit on F ²	1.043	1.034
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0369, wR ₂ = 0.0987	R ₁ = 0.0540, wR ₂ = 0.1114
Final R indexes [all data]	R ₁ = 0.0451, wR ₂ = 0.1044	R ₁ = 0.1010, wR ₂ = 0.1263
Largest diff. peak/hole / e Å ⁻³	0.36/-0.43	0.29/-0.20

Table S4. Bond lengths [Å] for **3·H₂O**.

parameter	Bond lengths [Å]	parameter	Bond lengths [Å]
C(1)-N(2)	1.3253(19)	C(6)-N(5)	1.359(2)
C(1)-N(1)	1.365(2)	N(1)-H(1A)	0.86
C(1)-C(2)	1.432(2)	N(1)-H(1B)	0.86
C(2)-C(6)	1.400(2)	N(2)-N(3)	1.3820(18)
C(2)-C(3)	1.408(2)	N(3)-H(3)	0.839(19)
C(3)-N(3)	1.3314(19)	N(4)-H(4A)	0.86
C(3)-C(4)	1.412(2)	N(4)-H(4B)	0.86
C(4)-C(5)	1.354(2)	N(5)-H(5)	0.81(2)
C(4)-H(4)	0.93	N(6)-N(7)	1.2486(19)
C(5)-N(5)	1.3747(19)	N(7)-N(8)	1.117(2)
C(5)-N(6)	1.4039(19)	O(1)-H(1C)	0.845(16)
C(6)-N(4)	1.3231(19)	O(1)-H(1D)	0.844(15)

Table S5. Bond angles [°] for 3·H₂O.

parameter	Bond angles [°]	parameter	Bond lengths [Å]
N(2)-C(1)-N(1)	121.69(14)	N(5)-C(6)-C(2)	116.29(13)
N(2)-C(1)-C(2)	110.42(13)	C(1)-N(1)-H(1A)	120
N(1)-C(1)-C(2)	127.76(14)	C(1)-N(1)-H(1B)	120
C(6)-C(2)-C(3)	119.20(13)	H(1A)-N(1)-H(1B)	120
C(6)-C(2)-C(1)	135.78(14)	C(1)-N(2)-N(3)	105.60(12)
C(3)-C(2)-C(1)	104.81(13)	C(3)-N(3)-N(2)	112.62(12)
N(3)-C(3)-C(2)	106.55(12)	C(3)-N(3)-H(3)	124.4(13)
N(3)-C(3)-C(4)	130.45(13)	N(2)-N(3)-H(3)	122.6(13)
C(2)-C(3)-C(4)	122.94(13)	C(6)-N(4)-H(4A)	120
C(5)-C(4)-C(3)	115.14(13)	C(6)-N(4)-H(4B)	120
C(5)-C(4)-H(4)	122.4	H(4A)-N(4)-H(4B)	120
C(3)-C(4)-H(4)	122.4	C(6)-N(5)-C(5)	124.12(13)
C(4)-C(5)-N(5)	122.27(13)	C(6)-N(5)-H(5)	118.2(13)
C(4)-C(5)-N(6)	127.90(13)	C(5)-N(5)-H(5)	117.2(13)
N(5)-C(5)-N(6)	109.83(13)	N(7)-N(6)-C(5)	114.60(13)
N(4)-C(6)-N(5)	117.72(14)	N(8)-N(7)-N(6)	172.14(16)
N(4)-C(6)-C(2)	125.99(14)	H(1C)-O(1)-H(1D)	110(2)

Table S6. Hydrogen bonds for 3·H₂O [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(4)-H(4A)...Cl(1)	0.86	2.46	3.2359(15)	151
N(4)-H(4B)...O(1)#1	0.86	2.42	3.047(2)	130.6
N(5)-H(5)...Cl(1)	0.81(2)	2.377(19)	3.1449(14)	157.5(17)
N(1)-H(1A)...N(2)#2	0.86	2.3	3.1346(19)	163
N(1)-H(1B)...O(1)#1	0.86	2.55	3.229(2)	137.1
C(4)-H(4)...Cl(1)#3	0.93	2.78	3.6615(15)	158.8
N(3)-H(3)...O(1)	0.839(19)	2.027(19)	2.8497(18)	166.5(19)
O(1)-H(1C)...Cl(1)#3	0.845(16)	2.322(15)	3.1466(15)	165(2)
O(1)-H(1D)...Cl(1)#4	0.844(15)	2.428(16)	3.2721(16)	179(2)

Symmetry transformations used to generate equivalent atoms:

#1 x, -y+1/2, z-1/2 #2 -x+1, -y, -z+1 #3 x, -y+3/2, z+1/2

#4 -x, -y+1, -z+1

Table S7. Torsion Angles [°] for 3·H₂O

parameter	Torsion Angles [°]	parameter	Torsion Angles [°]
C(1)-C(2)-C(3)-C(4)	177.57(13)	C(4)-C(5)-N(5)-C(6)	-0.8(2)
C(1)-C(2)-C(3)-N(3)	0.09(15)	C(4)-C(5)-N(6)-N(7)	5.5(2)
C(1)-C(2)-C(6)-N(4)	2.4(3)	C(6)-C(2)-C(3)-C(4)	2.1(2)

C(1)-C(2)-C(6)-N(5)	-176.37(15)	C(6)-C(2)-C(3)-N(3)	-175.42(12)
C(1)-N(2)-N(3)-C(3)	0.51(17)	N(1)-C(1)-C(2)-C(3)	-175.74(15)
C(2)-C(1)-N(2)-N(3)	-0.43(16)	N(1)-C(1)-C(2)-C(6)	-1.4(3)
C(2)-C(3)-C(4)-C(5)	-0.7(2)	N(1)-C(1)-N(2)-N(3)	175.82(14)
C(2)-C(3)-N(3)-N(2)	-0.37(16)	N(2)-C(1)-C(2)-C(3)	0.22(16)
C(2)-C(6)-N(5)-C(5)	2.1(2)	N(2)-C(1)-C(2)-C(6)	174.60(16)
C(3)-C(2)-C(6)-N(4)	176.20(15)	N(3)-C(3)-C(4)-C(5)	176.09(14)
C(3)-C(2)-C(6)-N(5)	-2.6(2)	N(4)-C(6)-N(5)-C(5)	-176.82(14)
C(3)-C(4)-C(5)-N(5)	0.1(2)	N(5)-C(5)-N(6)-N(7)	-174.12(13)
C(3)-C(4)-C(5)-N(6)	-179.48(14)	N(6)-C(5)-N(5)-C(6)	178.81(13)
C(4)-C(3)-N(3)-N(2)	-177.59(14)		

Table S8. Bond lengths [Å] for 5·H₂O

parameter	Bond lengths [Å]	parameter	Bond lengths [Å]
C(1)-N(1)	1.314(4)	N(2)-H(2)	0.86
C(1)-N(4)	1.386(4)	N(3)-H(3)	0.86
C(1)-C(6)	1.424(4)	N(4)-H(4A)	0.8215
C(2)-N(2)	1.338(4)	N(4)-H(4B)	0.8983
C(2)-C(6)	1.405(4)	N(4)-H(4B)#1	0.8983
C(2)-C(3)	1.406(4)	N(5)-H(5A)	0.86
C(3)-C(4)	1.347(4)	N(5)-H(5B)	0.86
C(3)-H(3A)	0.93	N(6)-N(7)	1.251(4)
C(4)-N(3)	1.373(4)	N(7)-N(8)	1.104(4)
C(4)-N(6)	1.398(4)	N(9)-O(2)	1.232(3)
C(5)-N(5)	1.322(4)	N(9)-O(3)	1.234(3)
C(5)-N(3)	1.354(4)	N(9)-O(1)	1.239(3)
C(5)-C(6)	1.409(4)	O(4)-H(4C)	0.96
N(1)-N(2)	1.369(3)	O(4)-H(4D)	0.96

Table S9. Bond angles [°] for 5·H₂O.

parameter	Bond angles [°]	parameter	Bond angles [°]
N(1)-C(1)-N(4)	120.7(3)	C(2)-N(2)-H(2)	123.6
N(1)-C(1)-C(6)	111.3(2)	N(1)-N(2)-H(2)	123.6
N(4)-C(1)-C(6)	128.1(3)	C(5)-N(3)-C(4)	124.4(2)
N(2)-C(2)-C(6)	106.1(3)	C(5)-N(3)-H(3)	117.8
N(2)-C(2)-C(3)	131.0(3)	C(4)-N(3)-H(3)	117.8
C(6)-C(2)-C(3)	122.9(3)	C(1)-N(4)-H(4A)	112.1
C(4)-C(3)-C(2)	115.5(3)	C(1)-N(4)-H(4B)	108.2
C(4)-C(3)-H(3A)	122.2	H(4A)-N(4)-H(4B)	111.1
C(2)-C(3)-H(3A)	122.2	C(1)-N(4)-H(4B)#1	108.19(9)
C(3)-C(4)-N(3)	122.1(3)	H(4A)-N(4)-H(4B)#1	111.1
C(3)-C(4)-N(6)	127.2(3)	H(4B)-N(4)-H(4B)#1	105.9

N(3)-C(4)-N(6)	110.7(2)	C(5)-N(5)-H(5A)	120
N(5)-C(5)-N(3)	118.0(3)	C(5)-N(5)-H(5B)	120
N(5)-C(5)-C(6)	126.0(3)	H(5A)-N(5)-H(5B)	120
N(3)-C(5)-C(6)	116.0(3)	N(7)-N(6)-C(4)	113.9(2)
C(2)-C(6)-C(5)	119.1(3)	N(8)-N(7)-N(6)	172.5(3)
C(2)-C(6)-C(1)	104.5(2)	O(2)-N(9)-O(3)	120.7(3)
C(5)-C(6)-C(1)	136.4(3)	O(2)-N(9)-O(1)	118.5(3)
C(1)-N(1)-N(2)	105.4(2)	O(3)-N(9)-O(1)	120.8(3)
C(2)-N(2)-N(1)	112.8(2)	H(4C)-O(4)-H(4D)	109.5

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z

Table S10. Hydrogen bonds for **5**·H₂O [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3A)...O(1)	0.93	2.45	3.147(4)	131.7
N(2)-H(2)...N(9)	0.86	2.61	3.455(4)	168.6
N(2)-H(2)...O(1)	0.86	2.28	2.993(3)	140.2
N(2)-H(2)...O(2)	0.86	2.21	3.040(3)	163.3
N(3)-H(3)...O(3)#2	0.86	1.97	2.830(3)	179.7
N(4)-H(4A)...N(6)#3	0.82	2.66	3.445(4)	159.3
N(4)-H(4A)...O(3)#4	0.82	2.51	2.985(3)	118.3
N(4)-H(4B)...O(4 ^a)#4	0.9	2.26	2.904(4)	128.7
N(4)-H(4B)...O(4 ^a)#5	0.9	2.02	2.897(4)	165
N(5)-H(5A)...O(2)#2	0.86	2.07	2.929(3)	178.2
N(5)-H(5B)...O(4 ^a)#4	0.86	2.08	2.875(4)	153.5
N(5)-H(5B)...O(4 ^a)#6	0.86	2.08	2.875(4)	153.5
O(4 ^a)-H(4C ^a)...N(4)#5	0.96	2.36	2.897(4)	114.7
O(4 ^a)-H(4C ^a)...N(8)	0.96	2.39	3.116(5)	132.2
O(4 ^a)-H(4D ^a)...O(1)	0.96	2.06	2.753(4)	127.3

Symmetry transformations used to generate equivalent atoms:

#1 x,-y+1/2,z #2 x,y,z-1 #3 x-1,y,z #4 x-1,y,z-1

#5 -x+1,-y,-z+1 #6 x-1,-y+1/2,z-1

Table S11. Torsion Angles [°] for **5**·H₂O

parameter	Bond lengths [Å]	parameter	Bond lengths [Å]
N1-C1-C6-C2	0.000(1)	N6-C4-N3-C5	180.000(1)
N1-C1-C6-C5	180.000(1)	C1-N1-N2-C2	0.000(1)
N2-C2-C3-C4	180.000(1)	C2-C3-C4-N3	0.000(1)
N2-C2-C6-C1	0.000(1)	C2-C3-C4-N6	180.000(1)
N2-C2-C6-C5	180.000(1)	C3-C2-N2-N1	180.000(1)
N3-C4-N6-N7	180.000(1)	C3-C2-C6-C1	180.000(1)
N3-C5-C6-C1	180.000(1)	C3-C2-C6-C5	0.000(1)
N3-C5-C6-C2	0.000(1)	C3-C4-N3-C5	0.000(1)
N4-C1-N1-N2	180.000(0)	C3-C4-N6-N7	0.000(1)
N4-C1-C6-C2	180.000(1)	C6-C1-N1-N2	0.000(1)
N4-C1-C6-C5	0.000(1)	C6-C2-N2-N1	0.000(1)
N5-C5-N3-C4	180.000(1)	C6-C2-C3-C4	0.000(1)
N5-C5-C6-C1	0.000(1)	C6-C5-N3-C4	0.000(1)
N5-C5-C6-C2	180.000(1)		

Thermal stability

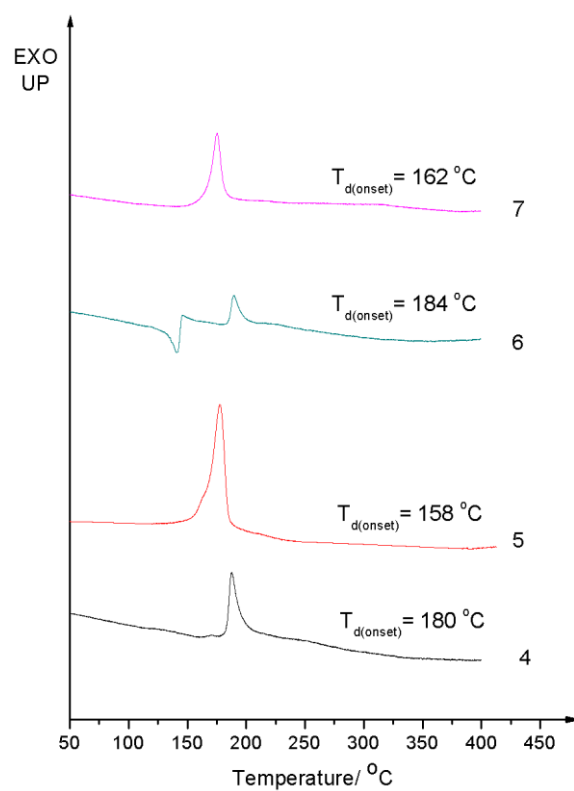


Figure S2. DSC plots for compounds 4-7

Spectral data

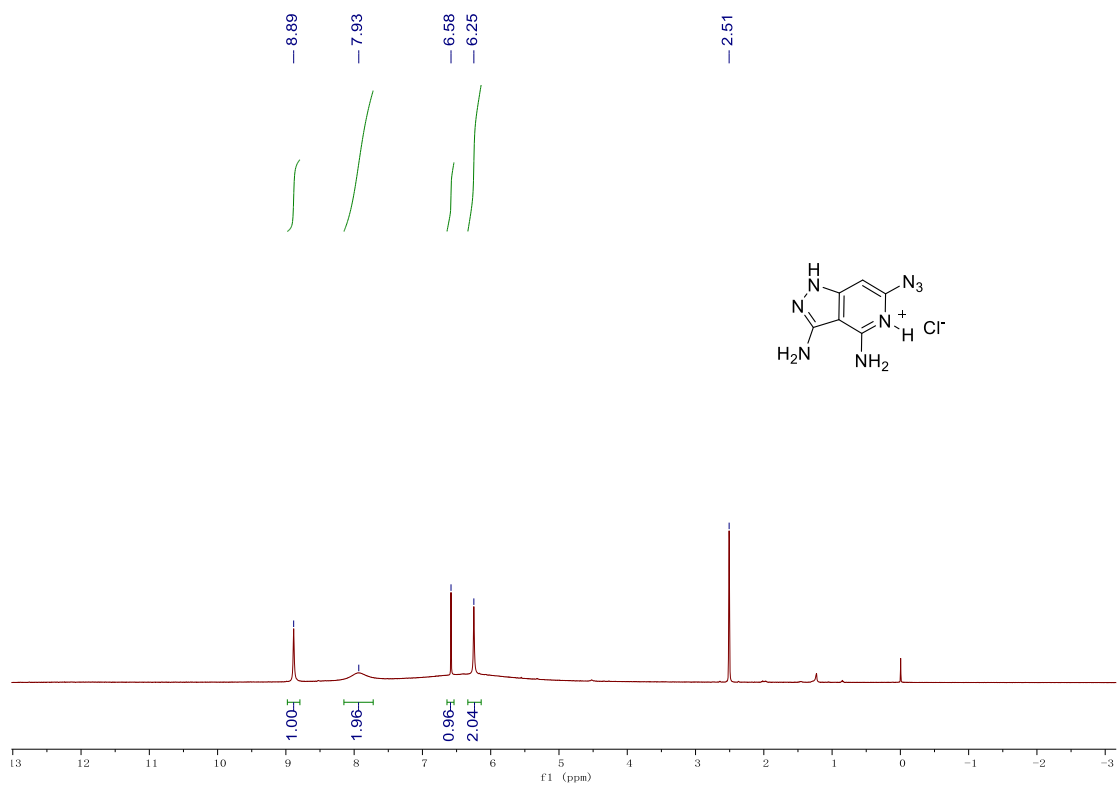


Figure S3. ¹H NMR spectra for compound 3

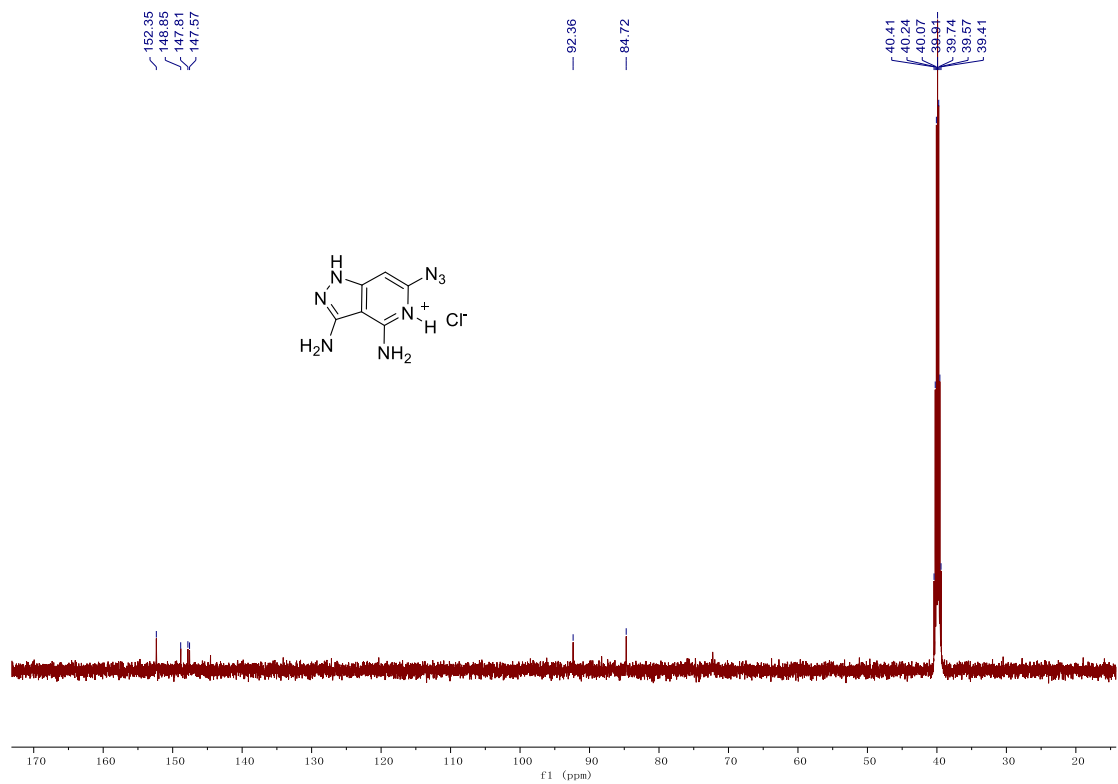


Figure S4. ¹³C NMR spectra for compound 3

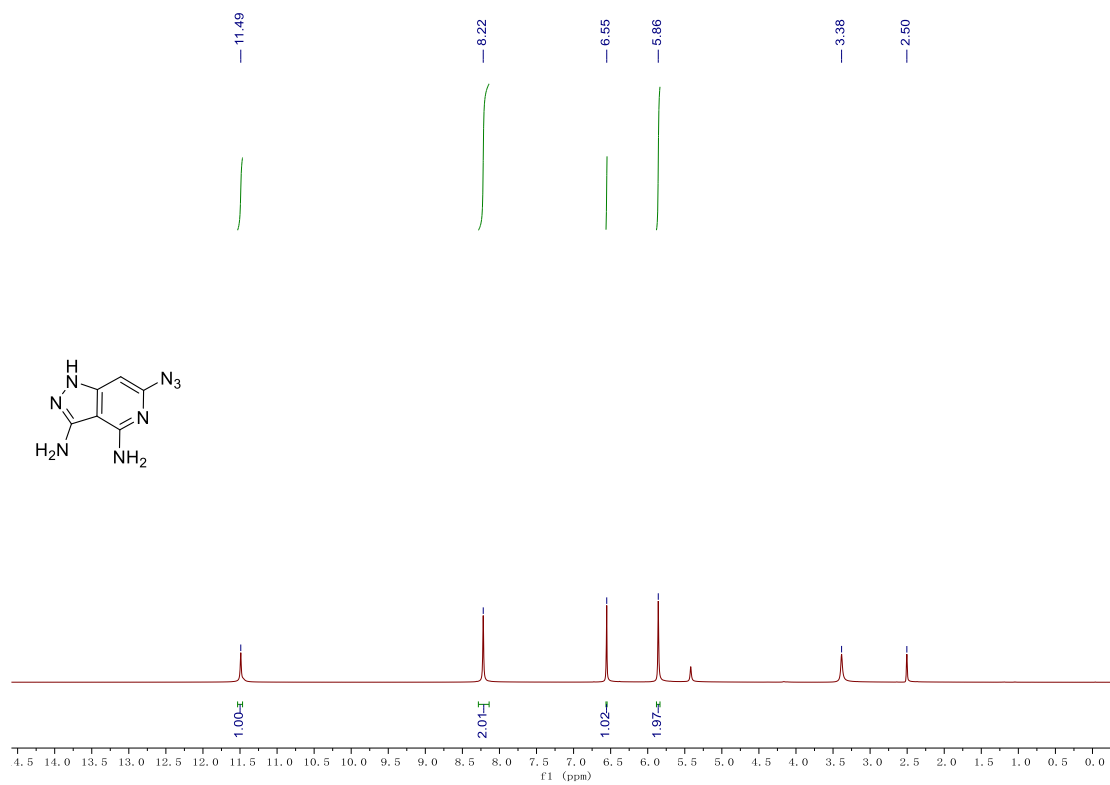


Figure S5. $^1\text{H NMR}$ spectra for compound 4

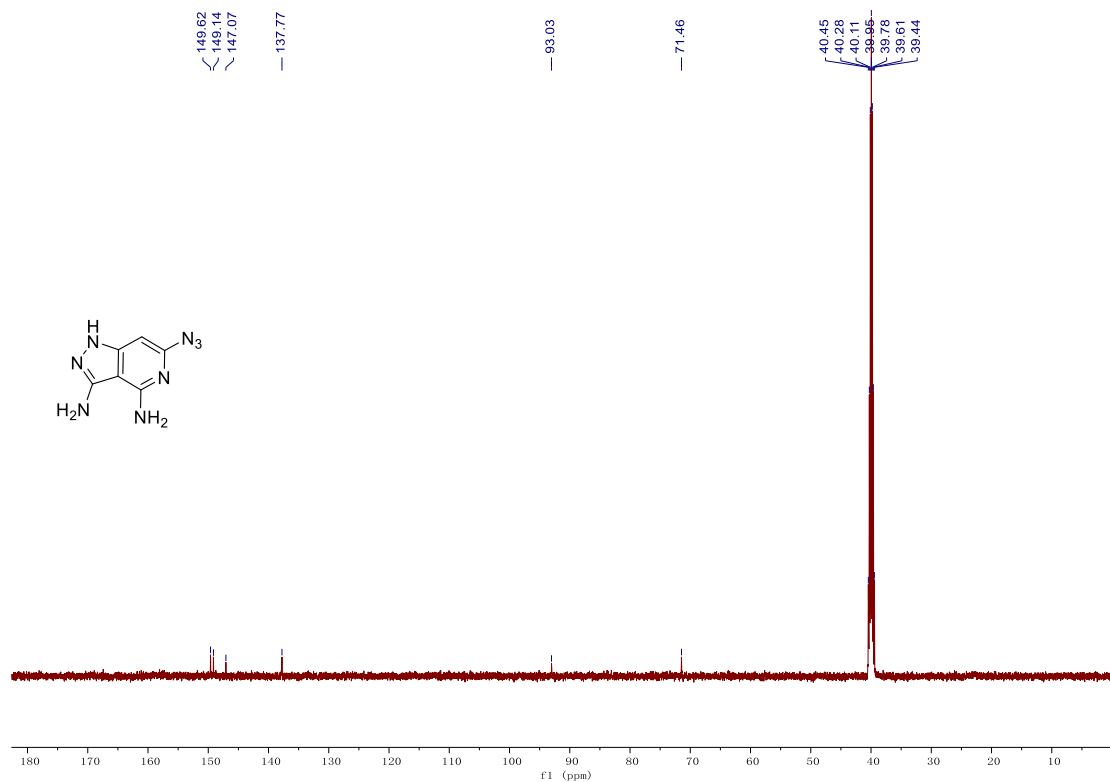


Figure S6. $^{13}\text{C NMR}$ spectra for compound 4

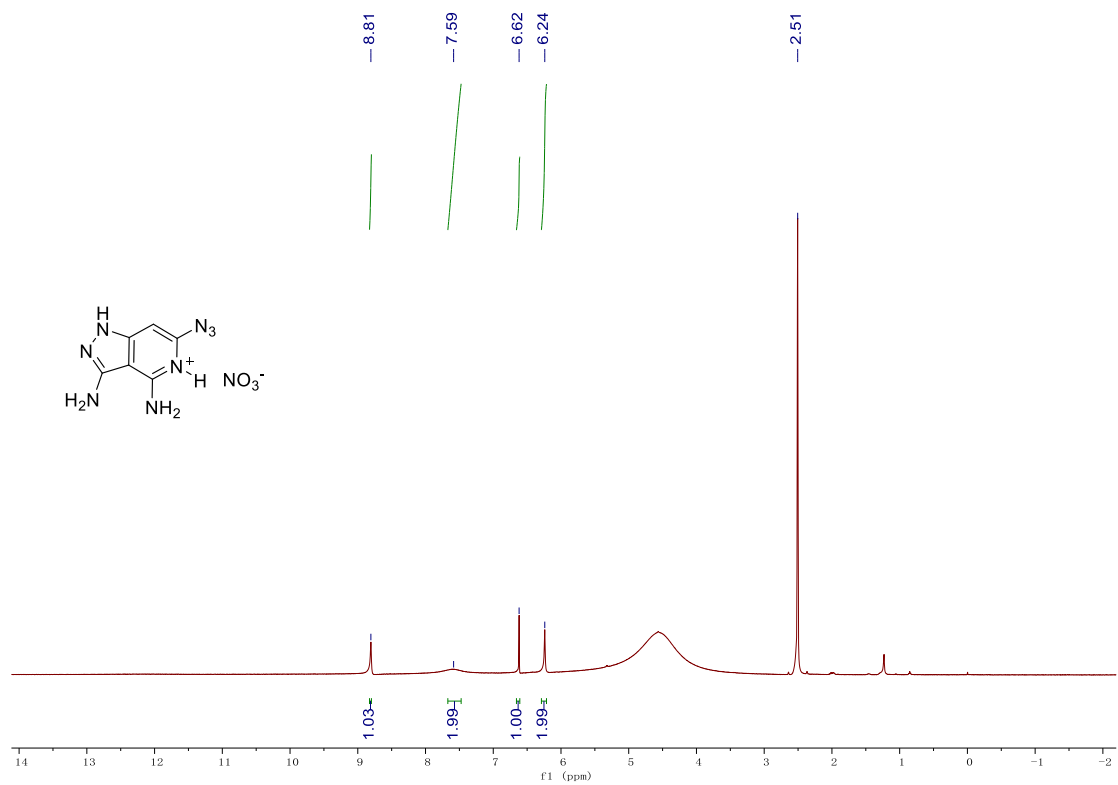


Figure S7. ¹H NMR spectra for compound 5

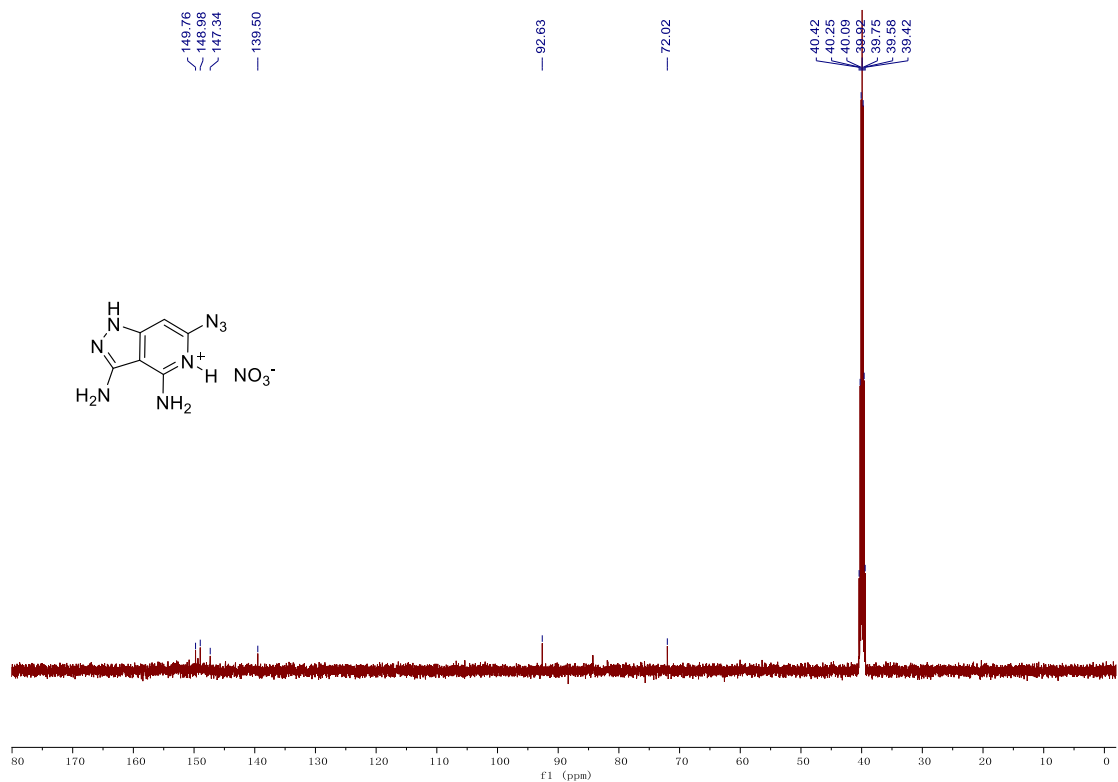


Figure S8. ¹³C NMR spectra for compound 5

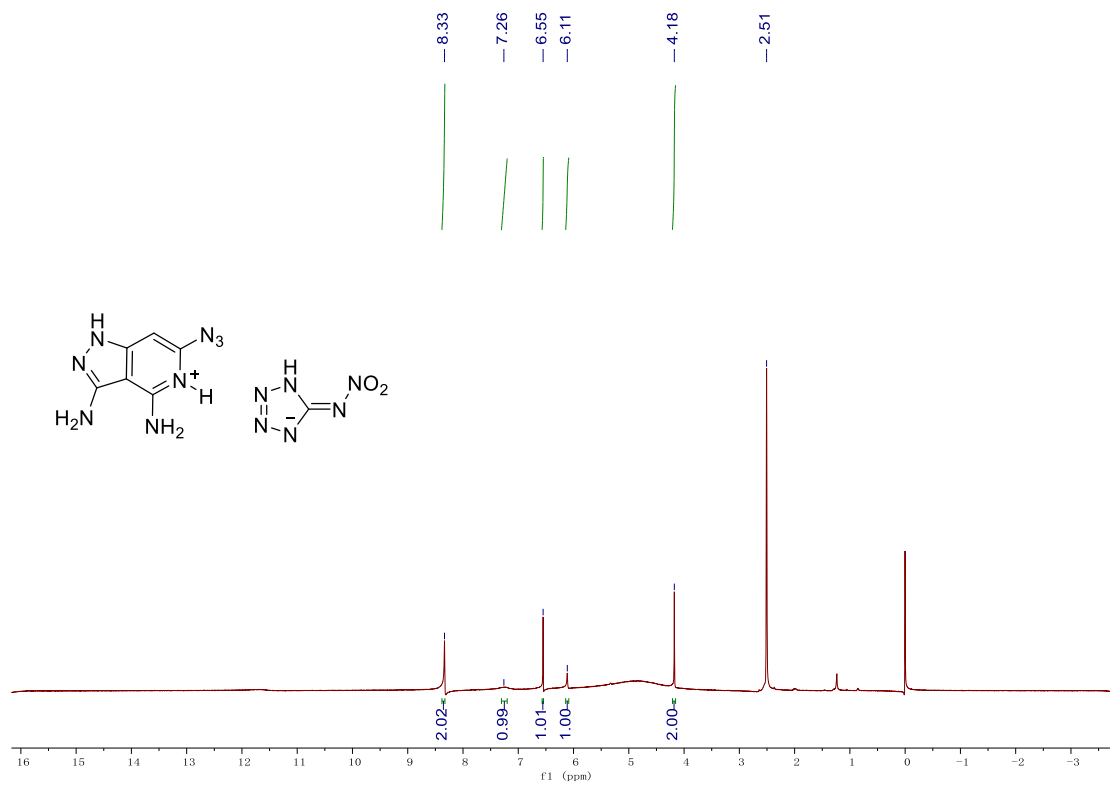


Figure S9. ^1H NMR spectra for compound **6**

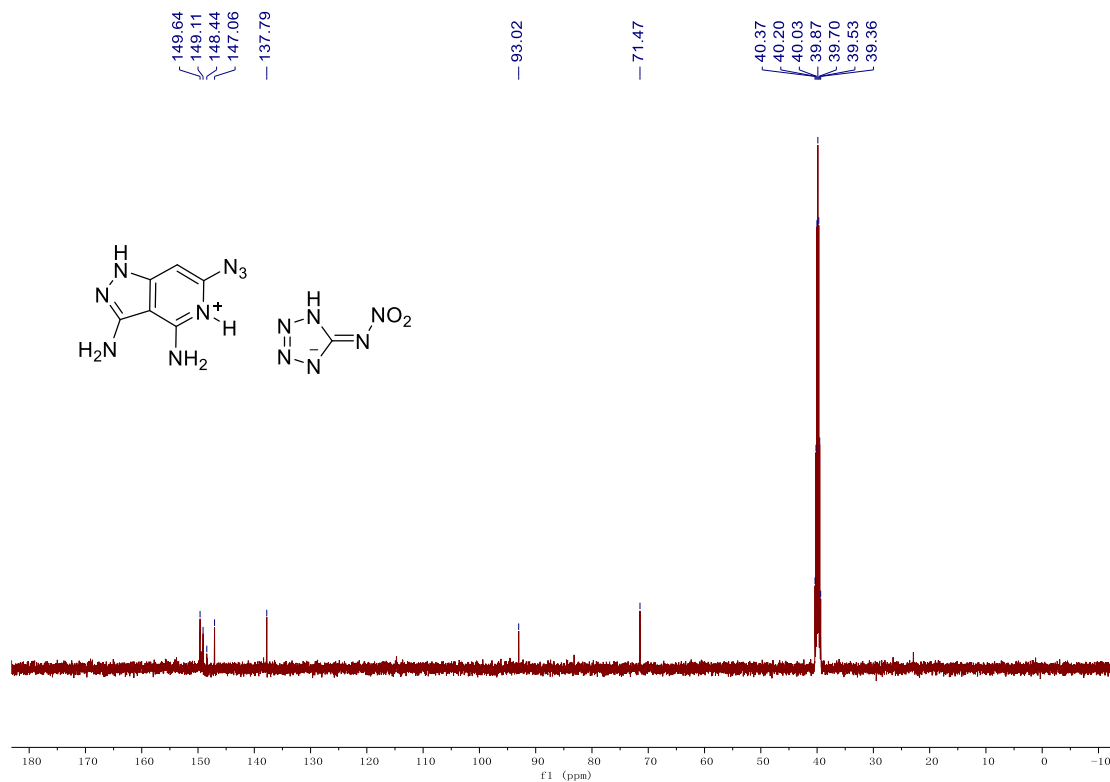


Figure S10. ^{13}C NMR spectra for compound **6**

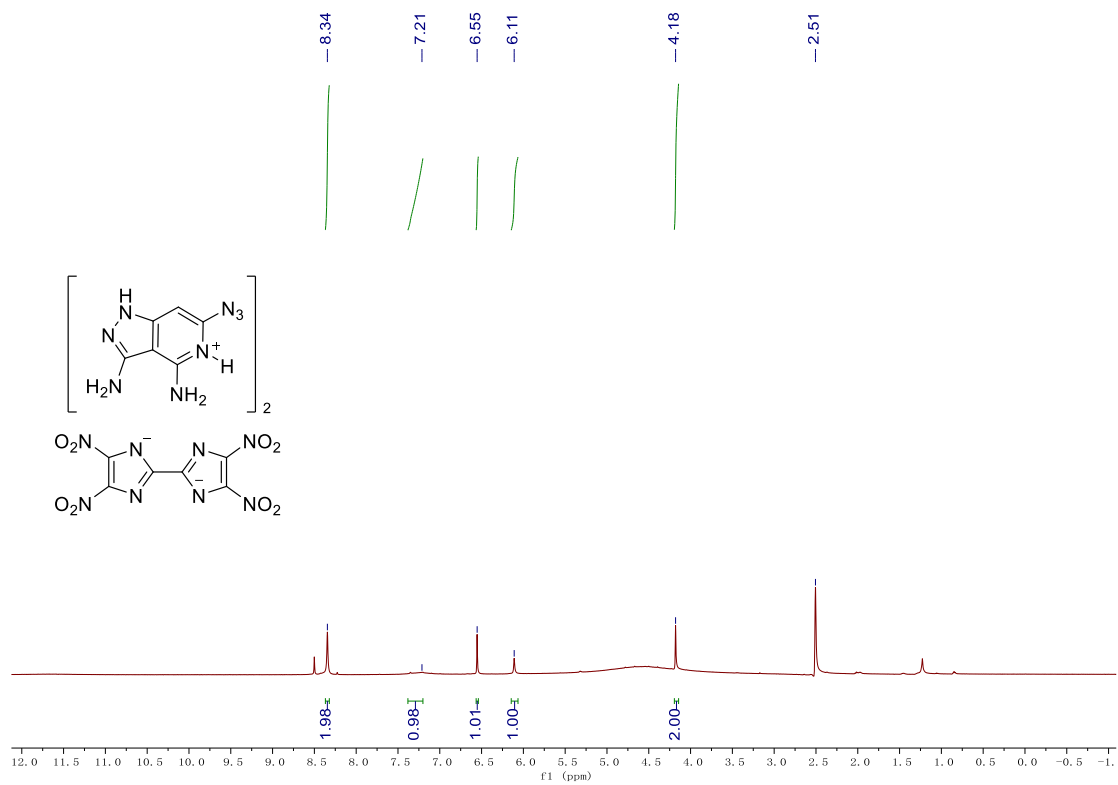


Figure S11. ¹H NMR spectra for compound 7

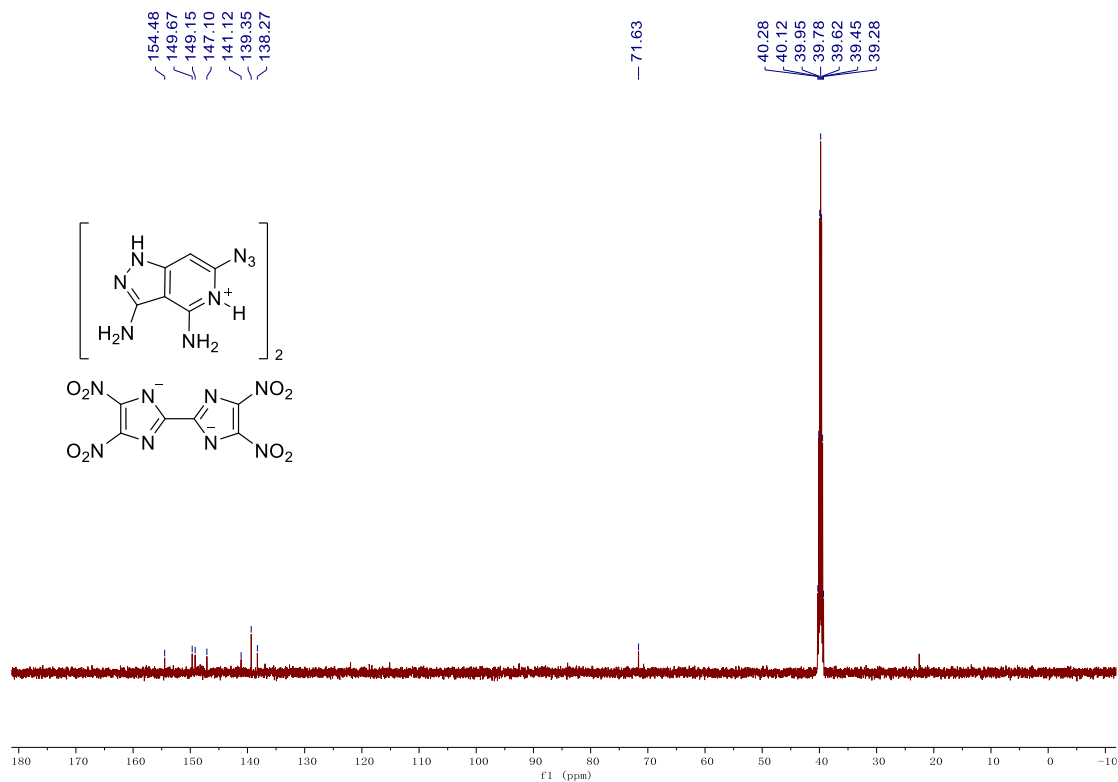


Figure S12. ¹³C NMR spectra for compound 7

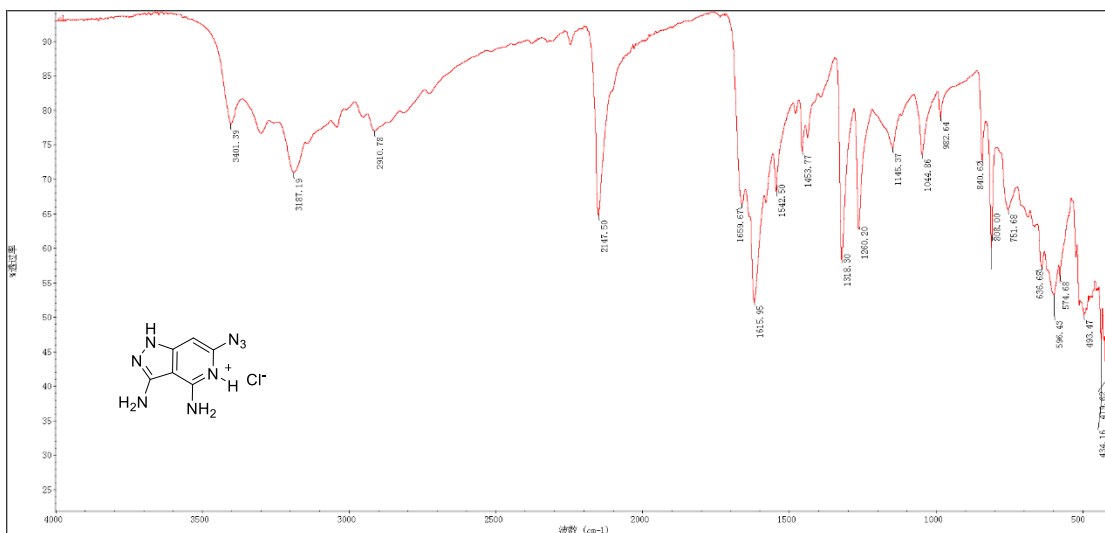


Figure S13. IR spectra for 3.

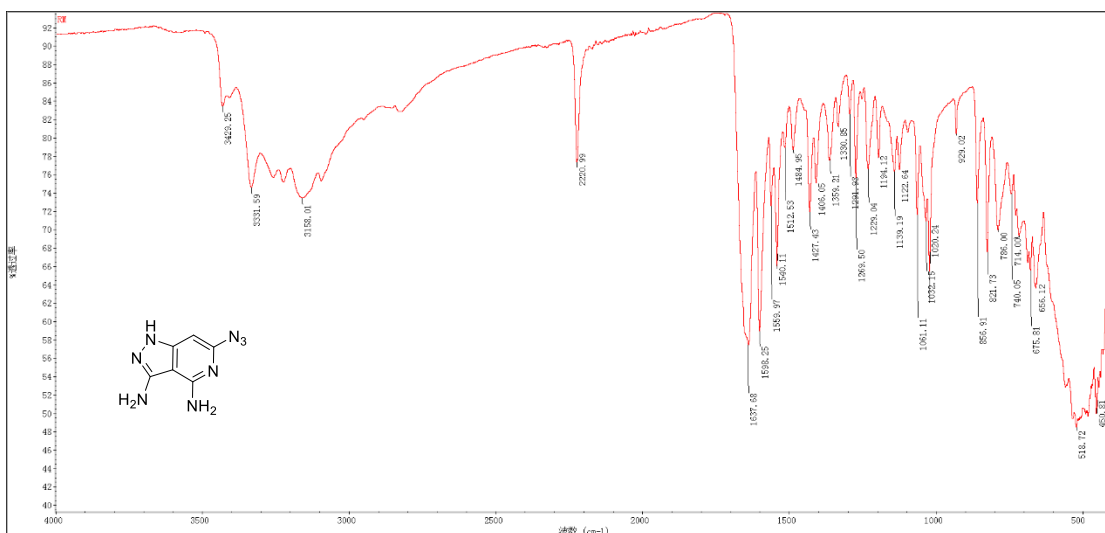


Figure S14. IR spectra for 4.

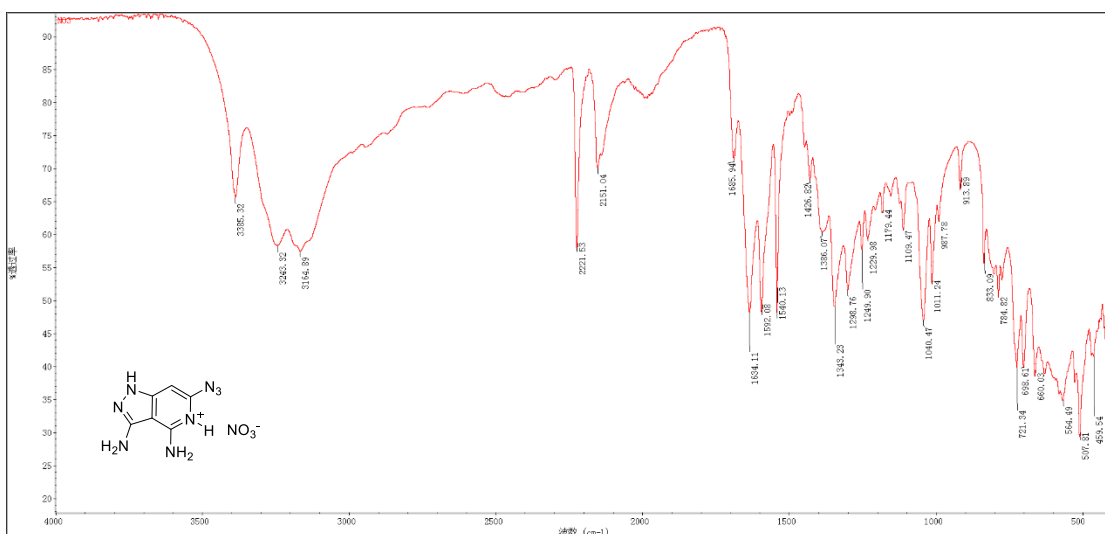


Figure S15. IR spectra for 5.

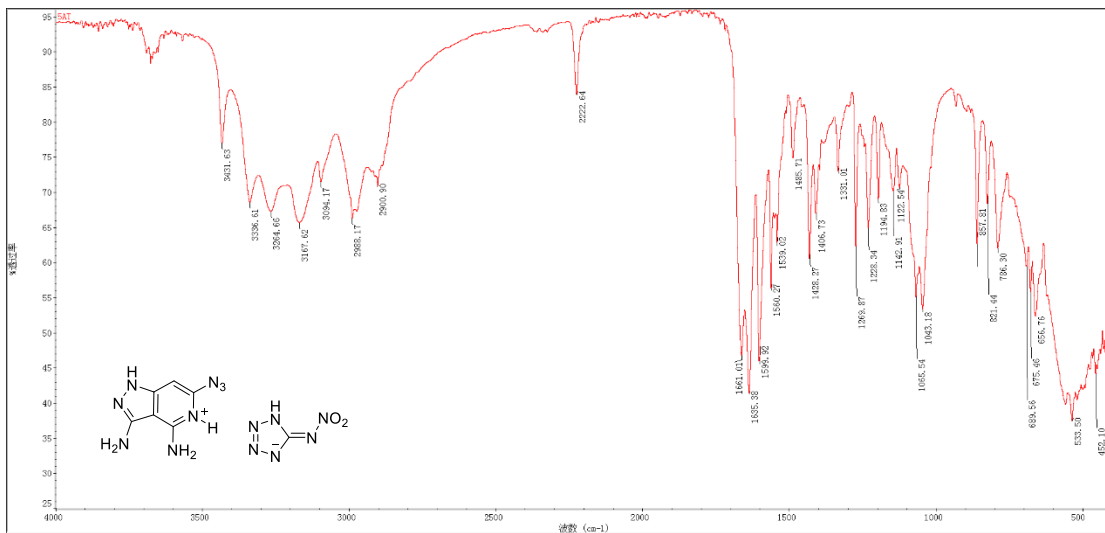


Figure S16. IR spectra for 6.

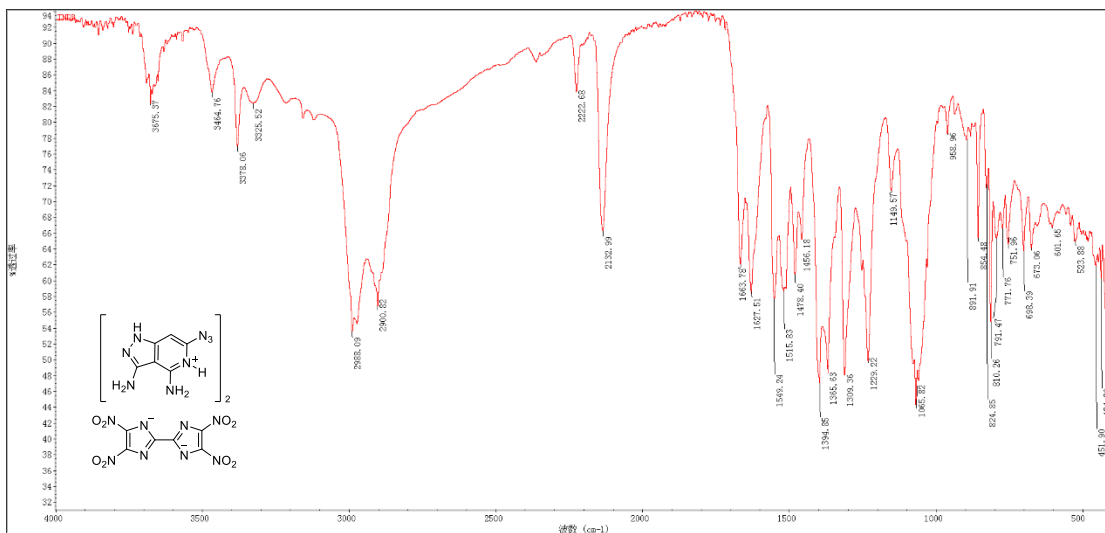


Figure S17. IR spectra for 7.

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, *Gaussian, Inc.*, Wallingford CT, 2009.
2. Y. Zhao and D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals, *Theor. Chem. Account.*, 2008, **120**, 215–241.
3. F. Weigend and R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297-3305.
4. H. D. B. Jenkins, D. Tudela and L. Glasser, Lattice potential energy estimation for complex ionic salts from density measurements, *Inorg. Chem.*, 2002, **41**, 2364-2367.
5. E. F. C. Byra and B. M. Rice, Improved prediction of heats of formation of energetic materials using quantum mechanical calculations, *J. Phys. Chem. A*, 2006, **110**, 1005-1013
6. H. Xiong, H. Yang and G. Cheng, 3-Trinitromethyl-4-nitro-5-nitramine-1H-pyrazole: A high energy density oxidizer, *New J. Chem.*, 2019, **43**, 13827-13831.